

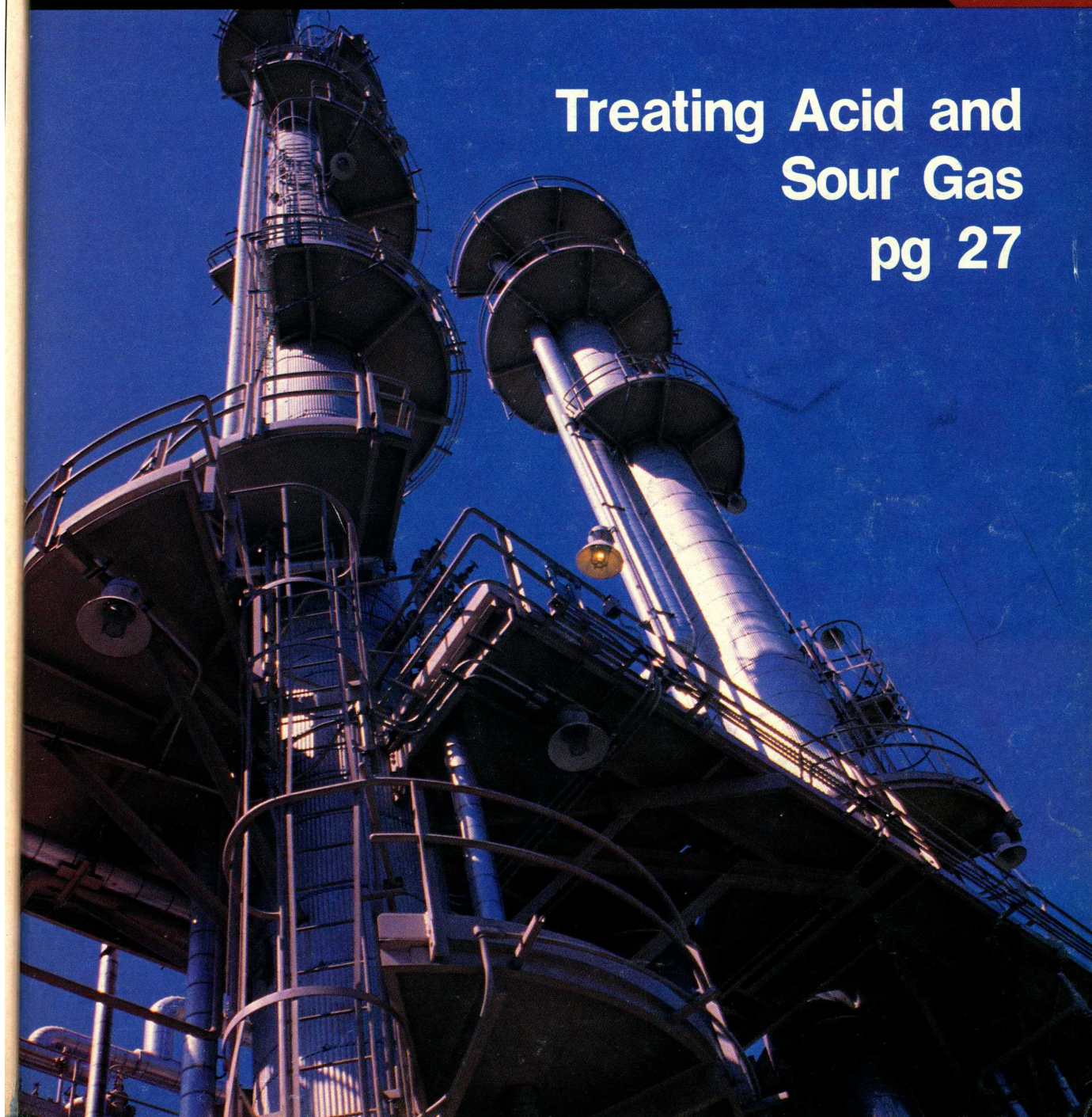
OCTOBER 1984

C&EP

**CHEMICAL
ENGINEERING PROGRESS**

1984
A YEAR OF
COMMUNICATION

**Treating Acid and
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Treating Acid & Sour Gas:

CO₂ Recovery by the Ryan/Holmes Process

This distillative approach economically recovers CO₂ and hydrocarbon liquids from natural gas streams.

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The Ryan/Holmes technology represents a unique, distillative approach to the recovery of CO₂ and hydrocarbon liquids from natural gas streams. It is a very flexible and economic solution to treating gas streams with very high CO₂ concentrations typically encountered with EOR (enhanced oil recovery) projects utilizing CO₂ injection. Recent experience has shown that appreciable cost savings can be realized in many EOR applications with a particular Ryan/Holmes four-column distillation sequence in contrast to the three-column arrangement discussed in previous articles.

Process principles

The Ryan/Holmes technology is a family of distillation separations using NGL-based additive introduced to the top or near the top of the distillation column. The additive, which is recycled from the bottom of a column in the distillation sequence, permits the desired separations to occur. Typically, the recycled additive is a butanes-plus mixture. All the distillations use conventional processing equipment.

The demethanizer column separates methane as an overhead product from CO₂, C₂, H₂S and C₃ and heavier hydrocarbons. Recycled additive is introduced to the condenser or to the top of the column to avoid freezing in the column. Only a small amount of additive is needed to avoid freezing. The relative volatility of C₁ to CO₂ is also improved by the presence of additive. The overhead C₁ fraction can be designed for 1 or 2% CO₂ as representative of pipeline-grade gas, or can be designed for 50 ppm CO₂ or lower suitable for feed to a liquefaction unit.

As more additive is circulated, the overhead of the demethanizer column becomes warmer as does the point of closest approach to freezing. Increased flow of additive can result in a demethanizer column where the coldest temperature is -35°F (-37°C), and the condenser cooling requirement can be accomplished by standard propane refrigeration systems. It should be noted that H₂S present in the feed is readily eliminated from the overhead C₁ product to levels below 1 ppm.

Ethane recovery columns are operated to produce a CO₂ overhead product and C₂, H₂S, C₃ and heavier hydrocarbons as a bottom product. The use of additive in this column breaks the azeotrope which forms between CO₂ and C₂. CO₂ and H₂S do not form an azeotrope, but on the CO₂-rich end the relative volatility is very poor. The additive functions to increase the relative volatility between CO₂ and H₂S. Additive is intro-

duced about ten trays down from the top of the column so as to provide a knock-back section at the top of the column which prevents the C₄+ additive from being carried into the CO₂ overhead product. The separation of CO₂ and C₂ or H₂S can be accomplished to any extent desired.

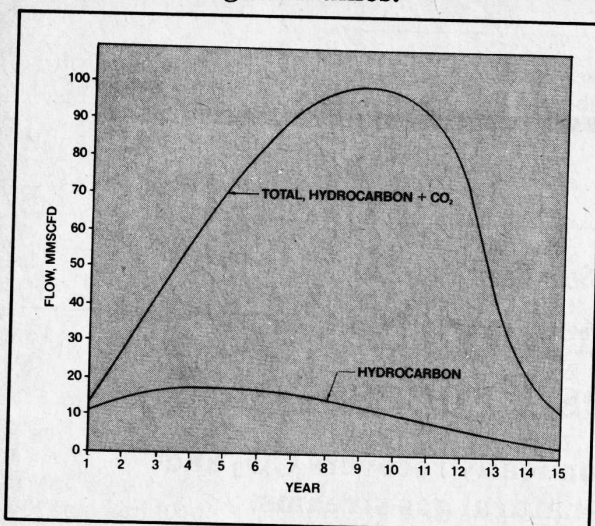
These basic separations have been tested in a pilot-plant program conducted with ARCO Oil and Gas at their Covington, Oklahoma gas, plant (1). Detailed studies of vapor-liquid equilibrium were conducted in phase equilibrium cells to obtain relevant data for the entire range of concentrations involved. The CO₂ pilot plant is now located at Koch's Corpus Christi refinery, where a program of further separation and column internal studies is in progress.

EOR gas-treating requirements

Enhanced oil recovery projects using CO₂ as a miscible injectant are being used extensively to recover additional oil from existing reservoirs. Typically, these projects involve injecting CO₂ into the formation on a schedule in which CO₂ injection and water injection are alternated in a so-called "WAG" operation. Oil production is stimulated by the presence of miscible CO₂. Concurrent with oil production rate increases, CO₂ is also produced because it is present in the oil and CO₂ "breakthrough" occurs. The separator gas requires processing to recover the valuable CO₂ for recycle as well as to eliminate CO₂ from the residue gas product and from recovered natural gas liquids. In many cases H₂S is also present in the formation. Gas processing is required to eliminate H₂S from the residue gas and from the CO₂ product.

A wide range of gas flows and compositions must be processed over the life of an EOR project. Figure 1 is a representative projection of the gas volumes to be processed over a period of 15 years. Usually, formations for which CO₂ injection are considered have a declining pattern of hydrocarbon gas volume production rate. After injecting CO₂, the hydrocarbon rate will climb, peak out and then resume a declining pattern. Along with the hydrocarbon gas, CO₂ is produced giving a total gas production rate which may increase quite considerably. In the example shown here, the total rate rises from about 15 MMSCFD (million standard ft³/d) (0.4×10^6 m³/d) at the beginning of the project to 100 MMSCFD (2.8×10^6 m³/d) nine or ten years later. The hydrocarbon gas volume increases by almost a factor of two and peaks out earlier than the CO₂ production. Of the hydrocarbon production, methane is typically less than 60% of the total and over the years declines as

Figure 1. Projected associated gas volumes.



SI Conversion: $m^3 = ft^3 \times 0.0283$

a fraction of the hydrocarbon gas. The NGL content of the hydrocarbon fraction increases over the years and may rise from values of 10–15 gal/MCF (thousand ft^3) (1.3–2.0 L/m^3) to values well over 20 gal/MCF (2.7 L/m^3). CO_2 content in the total gas volume will usually rise quickly to above 30 or 40% and often will spend many years at 70 to 90%. The gas processing plant built to handle a gas of such varying volume and composition must have a great deal of inherent flexibility.

Typical key specifications for the three products of an EOR gas processing facility are shown in Table 1. The methane product can be sold or used as fuel. Typically, in the early years there is an excess of methane required over the plant fuel needs which can be sold if it conforms to conventional sales gas specifications. Carbon dioxide content of the residue gas is therefore usually limited to about 2%, and H_2S is removed to the pipeline standard of $\frac{1}{4}$ grain/100 SCF (5.7 mg/m^3).

The key specifications for the CO_2 product typically include a limitation of about 4% methane and lighter constituents to maintain miscibility of the injectant at pressures well below the reservoir fracture limit. H_2S may be limited to 100 ppm for safety reasons. A pressure of approximately over 2,000 psig (14 MPa) is commonly needed for reinjecting the CO_2 .

NGL produced from a Ryan/Holmes facility will contain any H_2S present in the feed. In this regard, the requirement for the NGL product is that the CO_2 to H_2S ratio be less than 2 to 1. This makes the acid gas compatible with Claus unit operation without further selective separation. A conventional amine unit is able to remove the last of the acid constituents which can then be fed to the Claus unit.

Ethane recovery is typically specified between 60 and 90%. The limiting design condition may provide for a 60% recovery. When gas volume throughputs or the concentration of CO_2 is less, recoveries will rise to 90% or more. The recovery of propane and heavier hydrocarbons is essentially 100%.

Three-column scheme

The three-column Ryan/Holmes scheme (1, 2) consists of a demethanizer column, an ethane recovery column, and an additive recovery column in sequence, Figure 2. The demethanizer column and ethane recovery column are supplied with recycled additive to make possible the specified separations.

Table 1. Typical key specifications.

Sales Gas-Fuel	
CO_2	2%
H_2S	$\frac{1}{4}$ grain/100 SCF
550 psig	Pipeline or Fuel System
CO_2 Product	
C_1	4%
H_2S	100 ppm
2,200 psig	Reinjection
NGL Product (Sour)	
CO_2/H_2S	2/1
C_2 Recovery	90–60%

The demethanizer column separates the feed into a overhead fraction which is methane and lighter components such as nitrogen. The bottom product of the demethanizer is CO_2 , C_2 and heavier hydrocarbons including C_3 , C_4+ and additive. Any H_2S in the feed will be produced in the bottoms fraction.

In the ethane recovery column, CO_2 is produced as an overhead fraction. C_2 , H_2S , C_3 , C_4+ and additive are produced from the bottom of the column and flow to the additive recovery column. The role of the additive recovery column is to remove lighter NGL's to prevent them from being recycled. Butanes-plus is produced from the bottom of the column providing the net heavier NGL make and recovered additive to be recycled to the first two columns. H_2S , if present in the plant feed, will be produced in the overhead of the additive recovery column. The sour NGL's of the overhead are processed by conventional amine treatment to produce sweet NGL product.

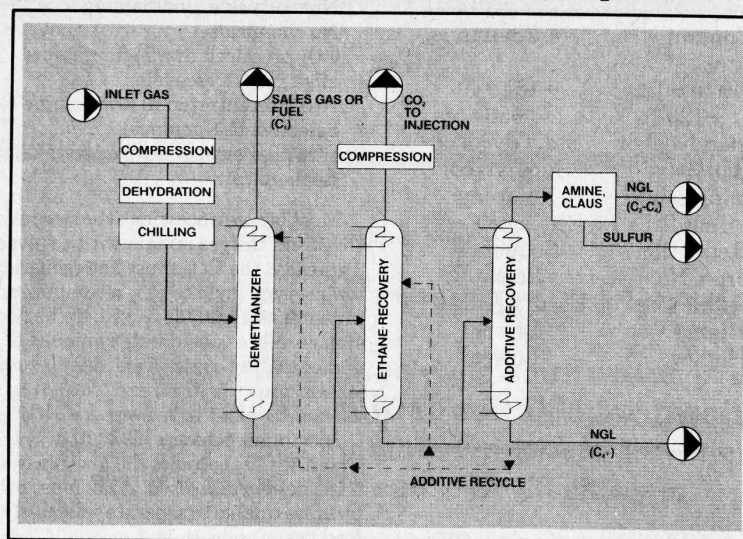
The additive column pressure is usually high enough to avoid the use of refrigeration and to permit overhead condensation by cooling water or aerial coolers. The temperature of the bottom of the additive column is typically the highest in the fractionating process. To some extent, this heat can be recovered by using the bottom stream as a reboiling medium in the ethane recovery column and the demethanizer column.

Four-column scheme

The major objectives which lead to the development of the four-column arrangement were to lower the energy consumption and capital cost of the overall processing scheme. After some study it became apparent that reducing the flow of additive and producing the CO_2 product as a liquid-column bottoms stream would help accomplish these objectives. If a liquid CO_2 product bottoms stream were to be produced, it would have to be from a column into which no additive was fed. Figure 3 shows the resulting four-column flow schematic.

The first column entered is the ethane recovery column in which the split between CO_2 overhead and a bottom product of C_2 , H_2S , C_3+ and additive is effected. The overhead is then compressed, chilled by refrigerant and fed to a new column which is designated the CO_2 recovery column. No additive is used in the CO_2 recovery column so the overhead cannot be a pure methane fraction but will contain 15 to 30% CO_2 , depending on specific conditions. However, the bottom product of the CO_2 recovery column is as free of methane as desired. The liquid bottom product can be readily pumped by conventional pumps to whatever pressures are required for reinjection.

Figure 2. Three-column Ryan/Holmes process.



The overhead from the CO₂ recovery column flows next to a demethanizer column similar to the demethanizer of the three-column scheme but with greatly reduced CO₂ content. Recycled additive is utilized to produce a sales gas quality fraction overhead. Less additive is required for the four-column scheme since much of the CO₂ has been removed in the CO₂ recovery column. The bottoms of the demethanizer contains CO₂-plus additive. The bottom stream could conceivably be fractionated to recover additive for recycle but that has proven to be unnecessary. The bottoms can be used to fulfill some of the additive requirement in the ethane recovery column, the remainder of that requirement being made up with fresh recycle additive; i.e., the additive which is used in the demethanizer is used again.

The bottoms from the ethane recovery column flow to the additive recovery column in which a light NGL-heavy NGL split is made. Typically, C₂ through some of the C₄ is taken

overhead including any H₂S, if present in the inlet gas. The remaining heavy NGL bottoms comprises additive recycle and NGL product make.

Three- vs. four-column approach

A general comparison between the three-column and the four-column processes is shown in Table 2. The first column seen by feed in the three-column process is run at a temperature of -40 to -120°F (-40 to -84°C). In the four-column process, the coldest conditions in the first column are -10 to +40°F (-23 to +4°C). Because the process tends to fractionate water away from the cold process temperature zones, the dehydration processing required for the four-column scheme is not as severe. Dehydration for the three-column process should be to a -100°F (-73°C) dew point specification or even lower. In the case of the four-column process, the

Figure 3. Four-column Ryan/Holmes process.

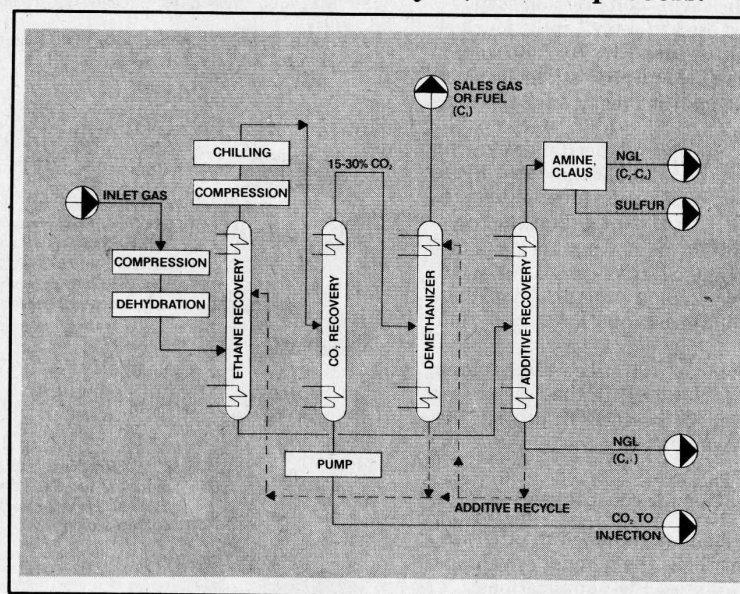


Table 2. Three- vs. four-column process.

	3 Column	4 Column
First Column, °F	-40 to -120	-10 to 40
Dehydration, °F	-120	-50
Dehydration Process	Superglycol or mol Sieve	Std. Glycol or Superglycol
CO ₂ Pressurizing	Compression	Pumping
CO ₂ Processing Sequence	Internal Pres. Reduction	Efficient Pres. Sequence
Additive	More—No "Double Use"	Less—Used "Double"
Reboiler Temp.	Higher	Lower
Power, hp	Higher	Lower

SI Conversion: °C = (°F - 32)/1.8; kW = hp × 0.746.

dehydration objective can be a dew point of only -50°F (-46°C).

To obtain the required dehydration for a three-column process, the glycol will have to be superstripped, such as by gas stripping or alternatively by an azeotropic entrainer. Alternatively, molecular sieves may be used at a somewhat greater expense. With a four-column process, a less severe method can be used.

The sequence of CO₂ processing represents a major difference between three- and four-column processing. CO₂ is often 70-90% of the inlet gas in an EOR application. In the three-column method, the CO₂ in the feed is compressed to about 600 psig (4 MPa), chilled and liquefied before entering the demethanizer and leaves the demethanizer in the liquid phase. The pressure is then dropped to about 300-400 psig (2-3 MPa) in the ethane recovery column where the CO₂ is produced as an overhead vapor product. Pressurization of CO₂ in the three-column process is accomplished by compressing the overhead vapor product from the ethane recovery column. The four-column scheme avoids liquefying and revaporizing the CO₂ and steps the CO₂ up in pressure increments, and so avoids the pressure energy losses inherent in the three-column approach. In the four column process, CO₂ pressurization is accomplished by pumping the liquid bottoms product of the CO₂ recovery column, thereby saving compression costs.

To some degree, additive is used "doubly" in the four-column method. Reboiler temperatures in the four-column process are lower than the three-column process which reflects the lower quantity of recycle additive needed for the four-column case.

The conclusion derived from several specific designs for EOR applications shows that the total horsepower (process compression, refrigeration compression, and pumping) for the four-column method is about 75% of the total for the three-column method. Heating medium energy input is about 65% of the three-column process, and additive circulation is 60% of that required for the three-column process. All of these factors contribute to a more efficient and lower cost plant design.

For streams with lower CO₂ concentrations three column processing might be favored. However, in the case of processing-associated gas from a CO₂-based EOR project, the four column method is the clear winner.

Advantages of Ryan/Holmes technology

Comparison of the Ryan/Holmes approach to other processing schemes serves to highlight the distinct advantages of the distillative approach for most EOR applications:

Flexible, reliable distillation
Feed dehydration by TEG
Noncorrosive, nonfoaming
No chemicals
CO₂ produced dry, high pressure
High NGL's recovery
H₂S concentrated in low-volume NGL stream
Selective H₂S removal
CO₂/H₂S ratio controlled for Claus feed
Economical

Most other processing schemes involve first absorbing the CO₂ from the gas stream with a solvent having CO₂ affinity. Typically, the CO₂ must be regenerated from the solvent at low pressure and the CO₂ recompressed to the high reinjection pressure required for recycle to the flood. This recompression step entails a considerable amount of additional investment and operating costs. Following CO₂ removal, the natural gas stream must be dried and treated in a conventional liquids extraction plant to recover the NGL product.

Membrane schemes also suffer from the same disadvantage since the CO₂ becomes the low-pressure permeate stream and must be recompressed. Also, most other processing alternatives are unable to separate selectively any H₂S present in the feed gas.

Flynn (3), in the comparison of various process routes for recycling CO₂ from an EOR project, determined the basic four-column Ryan/Holmes approach to have the lowest cost. As a result, Shell opted to license the Ryan/Holmes technology for the Wasson Denver unit in West Texas. However, Shell did elect to use their own selective H₂S absorption process prior to feeding the gas to the Ryan/Holmes portion of the plant.

Presently, Koch Process Systems has licensed four applications of the Ryan/Holmes technology. These include: the Seminole Unit operated by Amerada Hess; the Willard Unit, Wasson Field, operated by ARCO Oil and Gas (4); the GMK South Field operated by Mobil Producing Texas and New Mexico, Inc.; and the Wasson Denver Unit operated by Shell Oil. Its application is being actively considered by several other projects.

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